A Relationship between Thermal Diffusivity and Finite Deformation in Polymers[1]

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Abstract

The thermal diffusivity of elastomers, i.e. rubber-like materials, can with elastic finite deformation. Initially isotropic elastomers may be thermally anisotropic when deformed. Data from several experimental studies demonstrate significant changes in thermal conductivity or diffusivity tensor with finite deformation. Formulating the thermal diffusivity tensor and deformation in terms of the reference configuration may aid in the development of constitutive relation by use of material symmetry. Illustrated here is a relationship between the diffusivity and deformation of representative material during uniaxial and equibiaxial deformation. Each component of the diffusivity tensor appears to be related to the deformation in the direction of the component only. This simple correlation also seems to describe well changes in diffusivity in initially anisotropic elastomers and cold drawn semi-crystalline polymers.

1 INTRODUCTION

Elastomers are rubber-like materials that are often used in automotive, aerospace, and medical applications in conditions of severe thermal and mechanical stress. Designs incorporating elastomers and other engineering materials rely increasingly on computer models of material performance, thus requiring constitutive relations for the various responses of each material. Specifically thermomechanical models of elastomeric material responses require constitutive models for both the mechanical and thermophysical responses of these materials to various boundary conditions. Unlike most materials, elastomers exhibit unique thermomechanical responses, such as the well-known Joule-Gough and thermoelastic inversion effects. Few studies have examined the effect of temperature on mechanical response of elastomers, focusing instead on the isothermal response. Even fewer have examined the influence of deformation on the thermal response of elastomers. Some experiments have shown that there can be significant changes in the thermal conductivity or diffusivity tensors of elastomers subject to finite deformation. Broerman et al. [1] have measured, for example, increased thermal diffusivity in the direction of stretch for initially isotropic silicone rubber, while the diffusivity in the orthogonal direction decreases during uniaxial stretching. Results from uniaxial stretching experiments may demonstrate a given phenomenon, but are

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insufficient to develop constitutive models for multiaxial behavior. Constitutive relations for simple materials undergoing multiaxial deformation may be formulated from measurements of homogeneous multiaxial deformations [4]. LeGall and Wright [2] measured the three orthogonal components of the diffusivity tensor during biaxial stretching of polyurethane, natural gum and neoprene rubber. The deformation was homogeneous in the central region of the specimen, where the diffusivity was measured.

Constitutive relations for the thermophysical response of elastomers may be formulated in terms of either the thermal diffusivity or conductivity tensors, which depend on temperature and deformation, in general. Although the effect of temperature level on the value of thermal diffusivity has been relatively well studied [3, 5], the effect of deformation on the value of thermal diffusivity tensor has not been fully explored. Previous experimental results that have demonstrated the deformation dependence of the thermophysical response have not been formulated in a rigorous mathematical framework as may be required to develop constitutive equations to predict the thermomechanical response with general multiaxial finite deformation. Here, examining the results of previous experimental studies suggests a form for a constitutive relationship between diffusivity and deformation. This relationship relies on transferring data measured in the current configuration of the material to the reference configuration and comparing the result with the right Cauchy-Green deformation tensor. In this manner, a simple relation between the components of the diffusivity tensor and the deformation is observed for several elastomers. Moreover, this relation appears to correlate the data for several semi-crystalline polymers that have undergone permanent deformation at below their glass transition temperature.

2 ANALYSIS

Theory reveals that two constitutive functions are required to describe the reversible finite strain thermomechanical behavior of elastomers and that these may be the Helmholtz Potential ψ and the spatial heat flux vector $\mathbf{q}$ [6]. Theory futher shows that $\psi = \hat{\psi}(\mathbf{F}, T)$ and $\mathbf{q} = \hat{\mathbf{q}}(\mathbf{F}, T, \nabla T)$, where $\mathbf{F}$ ($= \partial \mathbf{x}/\partial \mathbf{X}$) is the deformation gradient tensor, T the temperature, ∇T ($= \partial T/\partial \mathbf{x}$) the temperature gradient, $\mathbf{X}$ the position vector of a material particle in the reference configuration, and $\mathbf{x}$ the position vector of a material particle in the current configuration. Material frame indifference allows ψ to be written as $\psi = \psi(\mathbf{C}, T)$, where $\mathbf{C}$ ($= \mathbf{F}^T \mathbf{F}$) is the right Cauchy-Green deformation tensor. Stress-strain-temperature relations result from derivatives of ψ with respect to $\mathbf{C}$. For example, the Cauchy stress $\mathbf{t}$ may be calculated by

$$\mathbf{t} = \frac{2}{J}\mathbf{F}\frac{\partial \psi(\mathbf{C}, T)}{\partial \mathbf{C}}\mathbf{F}^T \qquad (1)$$

where $J = det\mathbf{F}$.

A widely accepted model of ψ is sought, although a number of models have been proposed and describe mechanical response for various boundary conditions [8]. These models of ψ have been developed based on either a statistical modeling of the molecular network or a phenomenological approach based on continuum mechanics. Treloar [7] provides details about development using statistical theory of the Gaussian model, also called the neo-Hookean. The Gaussian model was developed using insight into the chemical structure of elastomers to model the mechanical response and describes the mechanical response over a limited range of deformation. Conversely, the phenomenological method develops models of ψ based on

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a mathematically formal framework and continuum scale experimental results. It has been used to develop, for example, the neo-Hookean, Mooney-Rivlin, and Ogden models of the Helmholtz potential [8]. Little attention has been paid to the effects of temperature on the Helmholtz potential of elastomers, the focus being on isothermal deformation, instead. A notable exception is the study of the development of a secondary molecular network resulting from microstructral changes due to elevated temperature and deformation [9]. This new network results in changed mechanical response. Ogden [10] proposed a method for finding ψ as a function of biaxial stretches and temperature, whereas Humphrey and Rajagopal [11] showed that in-plane biaxial tests allow measurement of thermoelastic response functions (e.g., $\partial\psi/\partial I_C$ where $I_C = \text{tr}\mathbf{C}$) similar to the isothermal results of Rivlin and Saunders [12].

Alternatively, most conduction heat transfer analyses neglect the influence of finite strain on the heat flux vector. Rather, most reports assume Fourier conduction $\mathbf{q}(\mathbf{x}, T) = -k(T)\boldsymbol{\nabla}T$ where $\mathbf{q}(\mathbf{x}, T)$ is the spatial heat flux, $\boldsymbol{\nabla}T$ $(= \partial T/\partial\mathbf{x})$ the spatial gradient of temperature, and $k(T)$ the scalar (i.e., isotropic) spatial thermal conductivity [3]. If anisotropy is considered, then the heat flux may be written in the current configuration as $\mathbf{q}(\mathbf{x}, T) = -\mathbf{k}(\mathbf{F}, T)\nabla T$ where $\mathbf{k}(\mathbf{F}, T)$ is the spatial thermal conductivity tensor. For materials subject to small deformation, models of thermal response may be developed using either the current or reference configurations with indistinguishable results. Elastomers, however, are often subject to large multiaxial deformation and models of the thermal response of materials subject to large deformation should include changes in material properties due to the deformation. The thermal conductivity of elastomers can change as a result of the large strain and may develop thermal anisotropy [1]. Note that finite strain constitutive relations are more easily formulated in terms of the referential thermal conductivity $\mathbf{K}(\mathbf{C}, T)$, due to material symmetry. Also note that $\mathbf{q} = (1/J)\mathbf{F}\mathbf{q}_0$, where $\mathbf{q}_0$ is the heat flux vector in the reference configuration and $J = \det\mathbf{F}$. Fourier conduction in the reference configuration may be written as $\mathbf{q}_0(\mathbf{x}, T) = -\mathbf{K}(\mathbf{C}, T) \cdot \boldsymbol{\nabla_0}T(\mathbf{X}, T)$, where $\nabla_0 T$ $(= \partial T/\partial\mathbf{X})$ is the referential temperature gradient. Fortunately, one can thus infer $\mathbf{K}(\mathbf{C}, T)$ from the measurable $\mathbf{k}(\mathbf{F}, T)$ via $\mathbf{k}(\mathbf{F}, T) = (1/J)\mathbf{F} \cdot \mathbf{K}(\mathbf{C}, T) \cdot \mathbf{F}^{\text{T}}$.

Substituting Fourier's equation into the referential conservation of energy equation yields, neglecting the stress power and heat sources,

$$\partial T(\mathbf{X}, t)/\partial t = \boldsymbol{\alpha}_0(\mathbf{C}, T) : \nabla_0^2 T(\mathbf{X}, t) \tag{2}$$

where $\boldsymbol{\alpha}_0(\mathbf{C}, T)$ $(= \mathbf{K}(\mathbf{C}, T)/\rho_0 c_F(\mathbf{C}, T))$ is the referential thermal diffusivity tensor, in which ρ_0 is the referential mass density and c_F the referential constant deformation specific heat. Because elastomers are here assumed to be incompressible and c_F is insensitive to deformation [1], either the thermal diffusivity tensor or thermal conductivity tensor may be used to characterize changes in thermophysical response due to deformation. Thermal diffusivity is more easily measured by non-contact methods, which is benefit for measurement of $\boldsymbol{\alpha}$ in materials subject to finite deformation.

Broerman et al. [1] used Forced Rayleigh Scattering (FRS) to measure the thermal diffusivity of silicone rubber subject to uniaxial stretching. In FRS, a transient optical grating is formed in the material by a diffraction pattern that results from absorption of crossed laser beams [13]. This grating diffracts the light of a third laser that is not absorbed by the material. The time decay in the efficiency of diffraction allows calculation of the
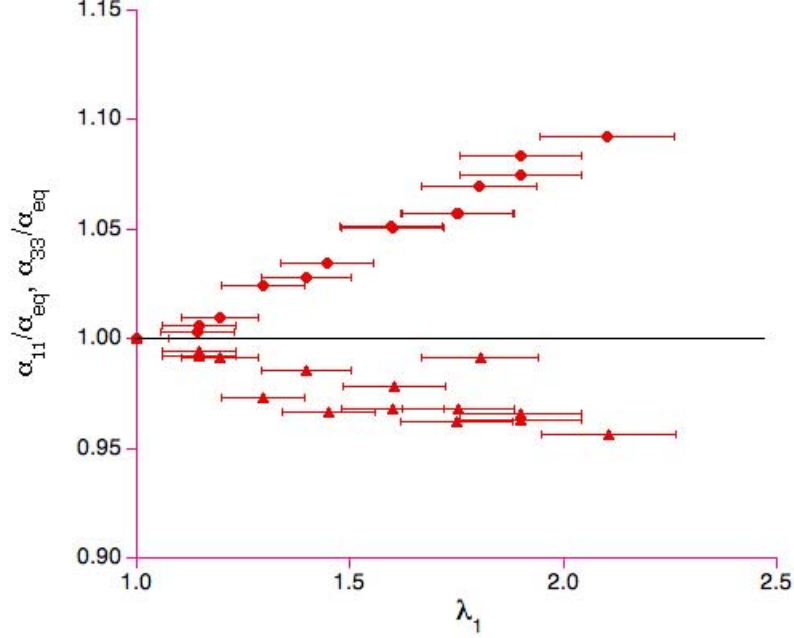
Figure 1: Diffusivity of silicone rubber subject to uniaxial stretching [1]. Circles are α_{11}, parallel to the stretch λ_1 and the triangles α_{33}, orthogonal to λ_1. The error bars represent $\pm 7.5\%$ uncertainty in the stretch measurement.

component of diffusivity in one direction. This method can measure one component of diffusivity at a time and requires the intersecting laser light to be absorbed by the material, which may require the material to be dyed. Nevertheless, the method can yield accurate measurements of thermal diffusivity. Figure 1 shows the variation of α_{11} and α_{33} for silicone rubber due to stretching in the 1-direction, as measured by Broerman et al. [1]. The error bars represent a $\pm 7.5\%$ uncertainty in the measured stretch. There appears to be a linear increase of α_{11} with respect to stretch ratio λ_1 which equals the current length divided by a reference length. A linear decrease appears in α_{33} with increasing λ_1. Prompted by the apparent linearity of the data, and inspired by the stress-optic rule, Broerman et al. describe their results using the stress-thermal rule [14], that is

$$(\alpha_{11} - \alpha_{33}) = c(t_{11} - t_{33}) \tag{3}$$

where c is a material parameter and the diffusivities are in the current configuration. This relation gives the trend of the difference between the components of diffusivity in this case of uniaxial stretching. The magnitude of each component is non-unique, however. Another approach might be to examine the relationship of α_{11} with respect to λ_1 and α_{33} with respect to λ_3. This requires computation of the orthogonal stretch, λ_3. Assuming material
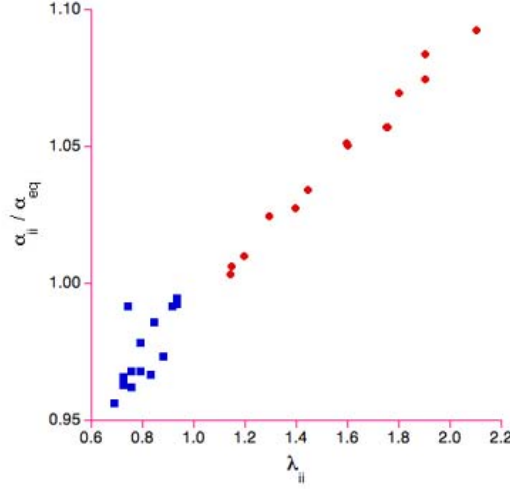
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Figure 2: The silicone rubber uniaxial loading data of Figure 1 replotted as α_{11} vs. λ_{11} (circles) and α_{33} vs. λ_{33} (triangles). The orthogonal stretch λ_{33} was calculated using incompressibility.

incompressibility $(J = 1)$, the deformation gradient tensor for uniaxial stretch is

$$
\mathbf{F} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda^{-1/2} \end{bmatrix}
\tag{4}
$$

and, thus, $\lambda_3 = 1/\sqrt{\lambda_1}$. Figure 2 shows the results of Broerman et al. in these terms for which there appears to be a single trend for $\boldsymbol{\alpha}$ in terms of α_{ii} as a function of the λ_i.

As mentioned above, to take advantage of possible symmetry conditions for initially isotropic materials, the values of $\boldsymbol{\alpha}$ should be transformed to $\boldsymbol{\alpha_0}$, i.e. the reference configuration. Likewise, deformation should then be described as $\mathbf{C}$ for constitutive modeling. Figure 3 the relationship between $\boldsymbol{\alpha_0}$ and $\mathbf{C}$ for silicone rubber in the reference configuration. The only non-zero components of $\boldsymbol{\alpha_0}$ are $\alpha_{0,11} = \alpha_{11}\lambda^2$, $\alpha_{0,22} = \alpha_{22}\lambda^{-1}$, and $\alpha_{0,33} = \alpha_{33}\lambda^{-1}$. Here, the material is assumed to be transversely isotropic, with $\alpha_{33} = \alpha_{22}$, consistent with Broerman et al. reporting only a single component of $\boldsymbol{\alpha}$ in the orthogonal direction. A least squares fit of these data shows that both the stretched and orthogonal directions apparently follow the same trend. This trend is described well by

$$
\frac{\alpha_{ii}}{\alpha_{eq}} = aC_{ii}^b \qquad i = 1, 2, 3 \qquad \text{(not summed)}
\tag{5}
$$

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Table 1: Coefficients for Equation 5 fit of $\boldsymbol{\alpha}/\boldsymbol{\alpha}_{eq}$ for initially isotropic elastomers subject to uniaxial or biaxial stretching.

Material	Loading	a	b	r^2	T	Ref
Silicone Rubber	Uniaxial	0.998	-0.945	0.990	25°C	[1]
PU RTV (preconditioning 1)	Biaxial	0.929	-0.926	0.998	20°C	[2]
PU RTV (preconditioning 2)	Biaxial	0.931	-0.946	0.998	20°C	[2]
PU RTV (preconditioning 3)	Biaxial	0.897	-0.929	0.998	20°C	[2]

where a and b are dimensionless material parameters, with values shown in Table 1.

LeGall and Wright [2] measured the principal components of thermal diffusivity of room temperature vulcanizing (RTV) polyurethane that was subject to homogeneous equibiaxial deformation, wherein both in-plane directions are stretched equally. They used a variation of the flash method [15] that measures the three principal components of $\boldsymbol{\alpha}$ simultaneously [16]. This pulse system involves a minimum of contact with the specimen, which is required for measuring the thermal diffusivity of materials undergoing finite stretch. For in-plane stretch ratios of λ_1 and λ_2, the out-of-plane stretch ratio will be $\lambda_3 = 1/\lambda_1\lambda_2$, for an incompressible material. The deformation gradient tensor is

$$\mathbf{F} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_1^{-1}\lambda_2^{-1} \end{bmatrix} \quad (6)$$

By again transforming $\boldsymbol{\alpha}$ to the reference configuration, and plotting the components of $\boldsymbol{\alpha_0}$ against the corresponding components of $\mathbf{C}$, there appears to be a single relationship for the polyurethane RTV (Figure 4). Least squares fitting of these data suggest a similar trend as in the uniaxial data. The coefficients for three specimens are listed in Table 1; LeGall and Wright [2] cite the three specimens separately because each had undergone a different mechanical preconditioning protocol. Preconditioning of elastomeric specimens is required to obtain repeatable thermoelastic results due to the Mullins effect [7].

4 DISSCUSSION

The isotropic thermal diffusivity tensor of undeformed elastomers develops anisotropy when the elastomer undergoes reversible finite strain. While constitutive relations for thermal diffusivity that include the influence of finite deformation could be developed using a number of coordinate frames, relating $\boldsymbol{\alpha}$ to $\boldsymbol{\alpha}_0$ and comparing it with $\mathbf{C}$, i.e., in the reference configuration, will aid in the development of the constitutive relations because of material symmetry. Equation 5 and its ability to fit the diffusivity data suggest that components of diffusivity are described by deformation in the same direction as that component, and are uninfluenced by deformation in the other directions. Deformation orthogonal to the uniaxial stretch or in the out-of-plane direction for the biaxial stretch case was computed assuming that rubber-like materials are volume preserving on deformation. This assumption has been well-justified based on measurements that have shown that volume changes are of the order
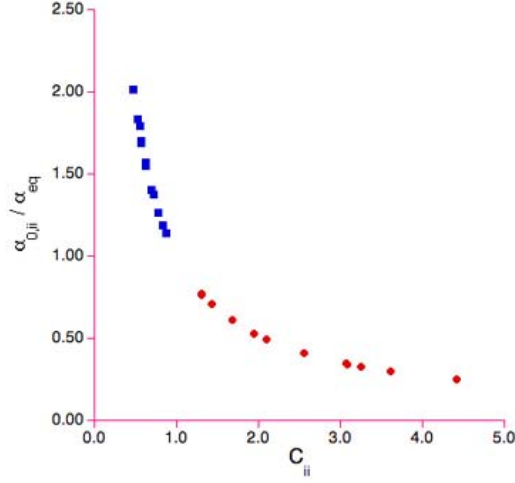
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Figure 3: Silicone rubber uniaxial loading data from Figure 1 plotted in the reference configuration as $\alpha_{0,11}$ vs. C_{11} (circles) and α_{33} vs. C_{33} (triangles).

10^{-4} or less [7]. Based on the assumption of incompressibility, the components of $\mathbf{F}$ are related by $J = 1$ and only one component of $\mathbf{F}$ is needed to characterize the deformation for the uniaxial and equibiaxial cases. This suggests that the off-axis terms are unlikely to contribute to changes in $\boldsymbol{\alpha}_0$ for initially isotropic materials.

Table 1 presents the coefficients for Equation 5 in terms of a normalized thermal diffusivity $\boldsymbol{\alpha}_0/\boldsymbol{\alpha}_{eq}$. In the study of Broerman et al., two components of thermal diffusivity are given, one parallel to the stretch direction and the other orthogonal to this direction, which implies that the $\boldsymbol{\alpha}$ is transversely isotropic after uniaxial stretch. The principal components of normalized thermal diffusivity from silicone rubber and polyurethane RTV shows that regardless of the deformation being uniaxial or biaxial, when examined in the reference configuration, the components of the thermal diffusivity tensor follow a similar trend with respect to the components of $\mathbf{C}$. The parameter a in Equation 5 would be expected to be 1 because when the material is undeformed, $\mathbf{F} = \mathbf{I}$ and $\mathbf{C} = \mathbf{F}^T\mathbf{F} = \mathbf{I}$, while, by definition, $\alpha_{ii} = \alpha_{eq}$. For silicone rubber, the coefficient a is about 1.0, which is consistent with above analysis. There is an approximately 8% deficit in a for the biaxially stretched polyurethane, however, which may suggest additional mechanisms and the need for a different correlation. The exponent b ranges approximately from -0.93 to -0.95 for both uniaxial and biaxial loading, somewhat different than a simple inverse relation. The implications of these parameter values and the variation with material formulation and sample loading warrant further study.
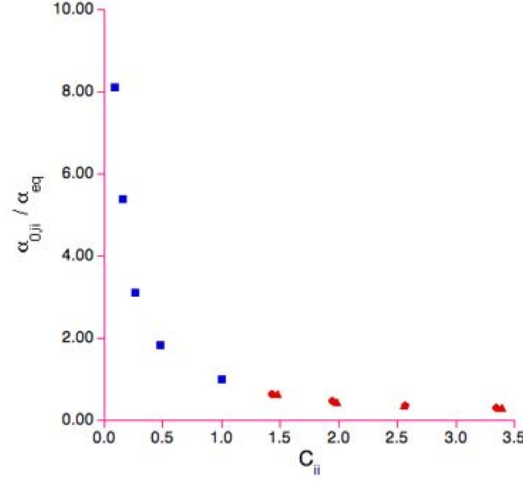
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Figure 4: Diffusivity of biaxially stretched polyurethane RTV rubber, in terms of the reference configuration. In-plane components are $\alpha_{0,11}/\alpha_{eq}$ vs. C_{11} (circles), $\alpha_{0,22}/\alpha_{eq}$ vs. C_{22} (squares), and $\alpha_{0,33}/\alpha_{eq}$ vs. C_{33} (triangles)
.

LeGall and Wright [2] also measured the principal components of $\boldsymbol{\alpha}$ of natural gum rubber (NGR) and neoprene that were anisotropic in the undeformed state due to manufacturing. In the reference state, the in-plane components of $\boldsymbol{\alpha}$ were 5 and 6 % higher than the out-of-plane coefficient for the NGR and neoprene, respectively. Materials with initial anisotropy exceed the assumptions of the aforementioned theoretical foundation for ψ and $\mathbf{q}$. Nevertheless, the response of these materials, shown by the values of a and b for the NGR and neoprene listed in Table 2, is similar to those listed in Table 1.

In addition to the elastomers, components of $\mathbf{k}$ have been measured for several polymers that were irreversibly drawn while cooler than their glass transition temperatures. As with diffusivity, $\mathbf{K}$ can be inferred from $\mathbf{k}$ and as before, the referential thermal conductivity and diffusivity tensors are related as $\boldsymbol{\alpha}_0(\mathbf{C}, T)(= \mathbf{K}(\mathbf{C}, T)/\rho_0 c_F(\mathbf{C}, T))$. Because of the assumption that the volume preserve during deformation, the density ρ would not change. In addition to that, the specific heat c_F would not change either during deformation [1], and thus $\boldsymbol{\alpha}_0/\boldsymbol{\alpha}_{eq} = \mathbf{K}/\mathbf{K}_{eq}$. Table 3 lists the coefficients a and b for high density polyethylene (HDPE), polymethylmethacrylate (PMMA), and polystyrene (PS). The PMMA and PS show similar behavior to the uniaxially stretched silicone rubber of Table 1, where as the HDPE behaves similarly to the biaxially stretched polyurethane, NGR, and neoprene.

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Table 2: Coefficients for Equation 5 for $\boldsymbol{\alpha}_0/\boldsymbol{\alpha}_{eq}$ of initially anisotropic elastomers subject to equibiaxial loading

Material	Loading	a	b	r^2	T	Ref.
NGR	Biaxial	0.9273	-0.9783	0.9943	20°C	[2]
Neoprene	Biaxial	0.9378	-0.9331	0.9948	20°C	[2]

Table 3: Coefficients for Equation 5 for $\mathbf{K}/\mathbf{K}_{eq}$ of polymers subject to uniaxial cold drawing.

Material	Loading	a	b	r	T	Ref.
HDPE	Uniaxial	0.863	-0.632	0.996	100 K	[17]
HDPE	Uniaxial	1.57	-0.591	0.942	300 K	[17]
PMMA	Uniaxial	1.01	-0.907	1.00	40°C	[18]
PS	Uniaxial	0.992	-0.988	1.00	40°C	[18]
PMMA (B-10834)	Uniaxial	1.00	-0.930	1.00	40°C	[18]
PMMA	Uniaxial	1.01	-0.901	1.00	40°C	[18]

5 CONCLUSION

There appears to be a simple relation between finite deformation and the changes in diffusivity of elastomers. Clearly, further study is required to clarify the relationship between $\boldsymbol{\alpha}$ and deformation for elastomers and other polymers. Additional theoretical developments will be needed to uncover the appropriate forms of ψ and $\mathbf{q}$ for drawn polymers, although these materials appear to follow a trend similar to the elastomers. Both molecular weight [18] and cross-linking [9] have influence on the thermomechanical response of elastomers. Their role on the constitutive behavior needs to be uncovered.

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